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(19) (CA) **CANADIAN PATENT** (12)

(54) MALODOR COUNTERACTANTS

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(21) APPLICATION No. 305,753

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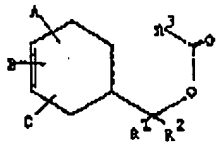
No. OF CLAIMS 36 - NO DRAWING

Abstract of the Disclosure

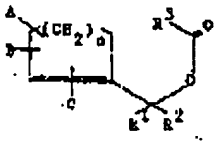
1107201

The compounds represented by the structural formulae



(1)

and



(2)

wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen, a lower alkyl having from 1 to 5 carbon atoms or a lower alkenyl having from 3 to 5 carbon atoms, provided that the sum of the carbon atoms in A, B and C is no more than 7,

R^1 and R^2 each independently represent hydrogen or a lower alkyl or alkenyl having from 1 to 5 carbon atoms,

R^3 represents hydrogen or a lower alkyl or alkenyl having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R^1 or R^2 plus R^3 is no more than 10,

have been found to be particularly useful in compositions and methods for counteracting malodors.

1107201

MALODOR COUNTERACTANTS

Cross-References to Related Applications

None.

Field of the Invention

This invention relates to the art of treatment of offensive odors, more particularly, to compositions and methods to counteract certain malodors.

Description of the Prior Art

The art of perfumery began, perhaps in the ancient cave dwellings of prehistoric man. From its inception, and until comparatively recently, the perfumer has utilized natural perfume chemicals of animal and vegetable origin. Thus, natural perfume chemicals such as the essential oils, for example, oil of rose and oil of cloves, and animal secretions such as musk, have been manipulated by the perfumer to achieve a variety of fragrances. In more recent years, however, research perfume chemists have developed a large number of synthetic chemicals possessing aroma characteristics particularly desired in the art. These synthetic aroma chemicals have added a new dimension to the ancient art of the perfumer, since the compounds prepared are usually of a stable chemical nature, are inexpensive as compared with the natural perfume chemicals and lend themselves more easily to manipulation than the natural perfume chemicals since such natural perfume chemicals are usually a complex nature of substances which defy chemical analysis. In contrast thereto, the synthetic aroma chemicals possess a known chemical structure and may therefore be manipulated by the perfumer to suit specific needs. Such needs vary over a very wide spectrum. Accordingly, there is a great need in the art of fragrance compositions for compounds possessing specific olfactory characteristics.

Heretofore a major effort in the art of perfumery has been directed to providing means of treating odors that are offensive to the human sense of smell. Such odors encompass a variety of odors such as bathroom-odor, kitchen-odor, body-odor, cigar smoke-odor, etc. Many products have been developed in an attempt to overcome these odors. So-called "room fresheners" or "room deodorants" are illustrative of such products.

In general these products have provided a masking effect by one of two mechanisms. The maskant fragrance is provided either to suppress the offensive odor by providing a more pleasing aroma in large quantities or by providing an aroma that blends with the offensive odor to provide a different and more desirable aroma. Unfortunately, in both instances a large amount of fragrance must be utilized which in itself often proves to be offensive. Furthermore, the offensive odor is usually still detectable at the levels of maskant fragrances that are reasonably tolerable. Accordingly, compositions and methods for counteracting such offensive odors which would substantially eliminate such odors without the above-noted disadvantages are particularly desirable.

Particularly noxious odors are caused by compounds which have a pronounced tendency to either donate or accept protons. Such compounds will hereinafter be referred to as "malodors". They include the olfactory notorious classes of lower carboxylic acids, thiols, thiophenols, phenols, lower amines, phosphines and arsines.

The compound 4-cyclohexyl-4-methyl-2-pentanone has heretofore been found to possess the ability to counteract such malodors. See U. S. Patent 4,009,253 issued February 22, 1977. See also my applications Canadian Serial No. 251,733, Canadian Serial No. 252,710 and Canadian Serial No. 293,102.

The following compounds have been described in the literature although their ability to counteract such malodors was undiscovered until the instant invention:

5-Methylcyclohex-3-en-1-ylmethyl methacrylate--Nordstrom, U. S. 3,536,687 issued October 27, 1970 (CA 74, P32769b)

3-(6'-Methylcyclohex-3'-en-1'-yl) prop-1-en-3-yl acetate--Kugatova et al., Zh. obsch. Khim. (1961) 31, 604 (CA 55,22175h)

3-(cyclohex-3'-en-1'-yl) prop-1-en-3-yl acetate--Kugatova et al., Zh. obsch. Khim. (1961) 31, 604 (CA 55,22175h)

1-(cyclohex-3'-en-1'-yl) propan-1-yl acetate--Petrov et al., J. gen Chem. USSR (1952) 22, 591 (CA 47,2736a)

1-(cyclohex-3'-en-1'-yl)-2,2-dimethylpropan-1-yl acetate--Kugatova et al., Zh. Organ. Khim. (1967) 3(7), 1220 (CA 67,90430a)

2-(4'-Methylcyclohex-3'-en-1'-yl) propan-2-yl acetate--Petrov et al., J. gen. Chem. USSR (1952) 22, 591 (CA 47,2736a)

2-(4'-Methylcyclohex-3'-en-1'-yl) propan-2-yl propionate--Kogami et al., Kogyo Kagaku Zasshi (1971) 74(11), 2304 (CA 76,34415y)

1-(cyclohex-3'-en-1'-yl) ethan-1-yl acetate--Petrov et al., J. gen. Chem. USSR (1952) 22, 591 (CA 47,2736a)

1-(cyclohex-3'-en-1'-yl)-2-methylpropan-1-yl acetate--Petrov et al., Zh. obsch. Khim. (1957) 27, 1795 (CA 52,4517a)

1-(Cyclohex-3'-en-1'-yl) pentan-1-yl acetate--Petrov et al., Zh. obsch. Khim. (1957) 27, 1795 (CA 52,4517a)

1-(Cyclohex-3'-en-1'-yl)-3-methylbutan-1-yl acetate--Petrov et al., Zh. obsch. Khim (1957) 27, 1795 (CA 52,4517a)

2,6,6-Trimethylcyclohex-1-en-1-ylmethyl acetate--Rudenko et al, Izvest, Ak. Nauk, SSSR, Otdel Khim. Nauk (1962), 236

2,6,6-Trimethylcyclohex-2'-en-1'-ylmethyl acetate--Smit et al., Izvest. Ak. Nauk. SSSR, Otdel Khim. Nauk (1959), 1848 (CA 54,8887g) and Smit et al., Izvest. Ak. Nauk. SSSR, Otdel Khim. Nauk (1962), 470 (CA 57,12541b)

4-(Cyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov et al., Zh. obsch Khim. (1963) 33(6), 1827 (CA 59,7384e)

4-(6'-Methylcyclohex-3'-en-1'yl) but-1-en-4yl acetate--Sopov et al., Zh. obsch. Khim (1963) 33(6), 1827 (CA 59,7384e)

1-(4',6'-Dimethylcyclohex-3'-en-1'-yl) butan-1-yl acetate--Sopov et al., Zh. obsch. Khim. (1963) 33(4), 1142 (CA 59,9827a) and Sopov et al., Zh. obsch. Khim. (1964) 34(5), 1492 (CA 61,5529d)

1-(4'-Methylcyclohex-3'-en-1'-yl) hexan-1'-yl acetate--Sopov et al., Zh. obsch. Khim. (1963) 33(4), 1142 (CA 59,9827a)

4-(2',6'-Dimethylcyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov et al., Zh. obsch. Khim. (1963) 33(4), 1142 (CA 59,9827a) and Sopov et al., Zh. obsch. Khim. (1964) 34(5), 1492 (CA 61,5529d)

4-(4'-Methylcyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov et al., Zh. obsch. Khim. (1964) 34(5), 1492 (CA 61,5529d)

4-(2'-Methylcyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov et al., Zh. obsch. Khim. (1964) 34(5), 1492 (CA 61,5529d)

1-(6'-Methylcyclohex-3'-en-1'-yl) butan-1-yl acetate--Sopov et al., Zh. Organ. Khim. (1965) 1(2), 233 (CA 62,14519g)

1-(6'-Methylcyclohex-3'-en-1'-yl)-2-methylpropan-1-yl acetate--Sopov et al., Zh. Organ. Khim. (1965) 1(2), 233 (CA 62,14519g)

1-(Cyclohex-3'-en-1'-yl) hexan-1-yl acetate--Sopov et al., Zh. Organ. Khim. (1965) 1(2), 233 (CA 62,14519g)

1-(6'-Methylcyclohex-3'-en-1'-yl) hexan-1-yl acetate--Sopov et al., Zh. Organ. Khim. (1965) 1(2), 233 (CA 62,14519g)

1-(6'-Methylcyclohex-3'-en-1'-yl) butan-1-yl acetate--Sopov et al., Zh. Organ. Khim. (1965) 1(2), 233 (CA 62,14519g)

1-(2',2',4'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate--Sopov, Zh. Organ. Khim. (1965) 1(3), 446 (CA 63,1712e)

4-(3',4'-Dimethylcyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov, Zh. Organ. Khim. (1965) 1(5), 827 (CA 63,6885a)

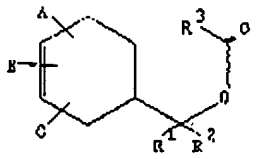
4-(3',4',6'-Trimethylcyclohex-3'-en-1'-yl) but-1-en-4-yl acetate--Sopov, Zh. Organ. Khim. (1965) 1(5), 827 (CA 63,6885a)

2-(Cyclohex-3'-en-1'-yl) propan-2-yl acetate--Ramaprabhu et al., Ind. J. Chem. (1972) 10(12), 1104

Summary of the Invention

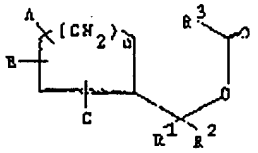
The present invention provides compounds and compositions which are especially useful in view of their ability to counteract malodors. Furthermore, novel methods are provided, i.e. the use of such compounds and compositions to counteract malodors.

The compounds which exhibit this surprising ability to counteract malodors are represented by the following structural formulae



(1)

and



(2)

wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen, a lower alkyl having from 1 to 5 carbon atoms or a lower alkenyl having from 3 to 5 carbon atoms, provided that the sum of the carbon atoms in A, B and C is no more than 7,

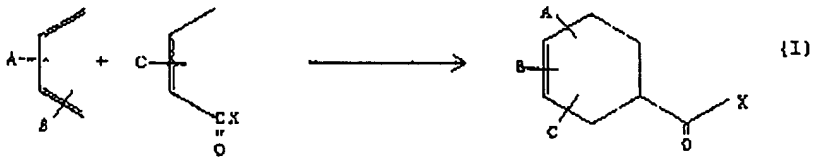
R^1 and R^2 each independently represent hydrogen or a lower alkyl or alkenyl having from 1 to 5 carbon atoms,

R^3 represents hydrogen or a lower alkyl or alkenyl having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R^1 or R^2 plus R^3 is no more than 10.

Description of the Preferred Embodiments

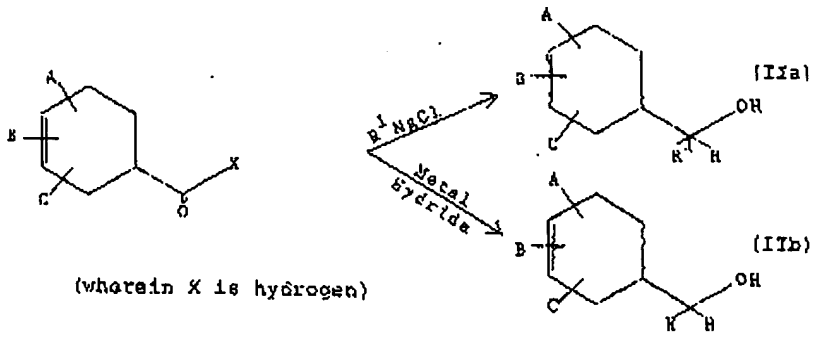
The term "counteract" as used herein means the effect on the human sense of smell and/or the malodor resulting in alleviating the offensiveness of the malodor to the human sense of smell. It is not intended that this term be limited to any particular mechanism by which such a result may be obtained.

The compounds of formula (I) useful in this invention can be prepared as illustrated by the following equations:



(I)

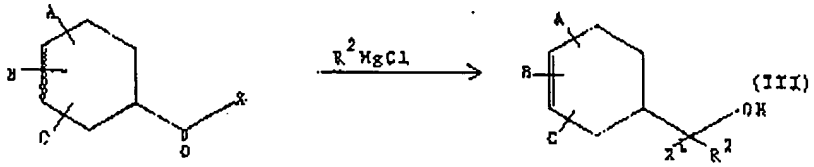
(wherein X is hydrogen, alkyl or alkenyl)



(IIa)

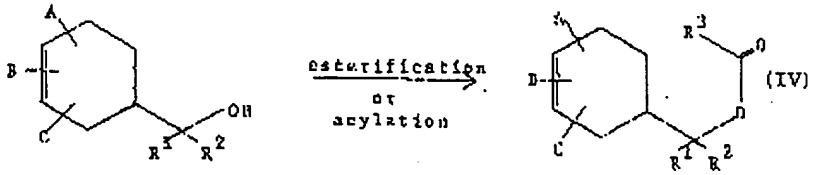
(IIb)

(wherein X is hydrogen)



(III)

(wherein X is alkyl or alkenyl (R^1))

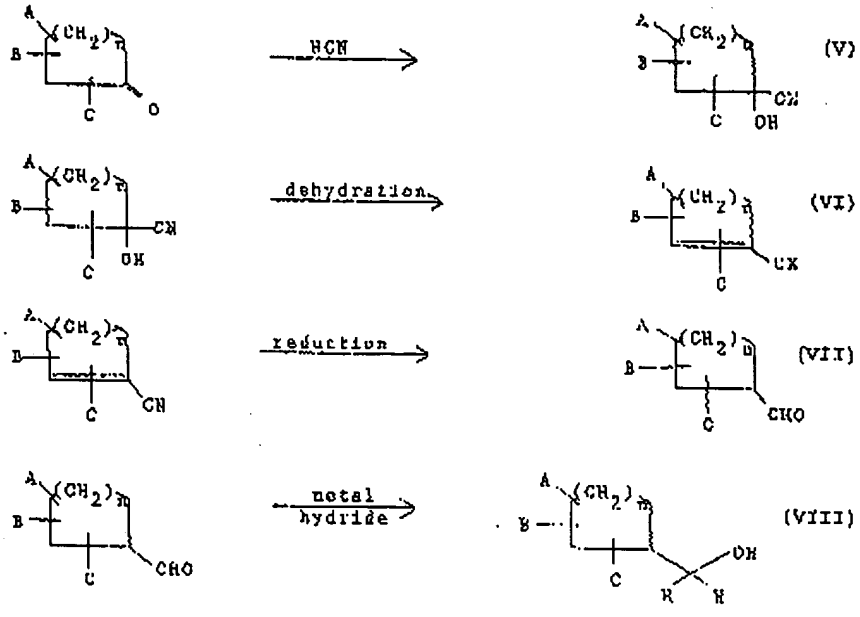


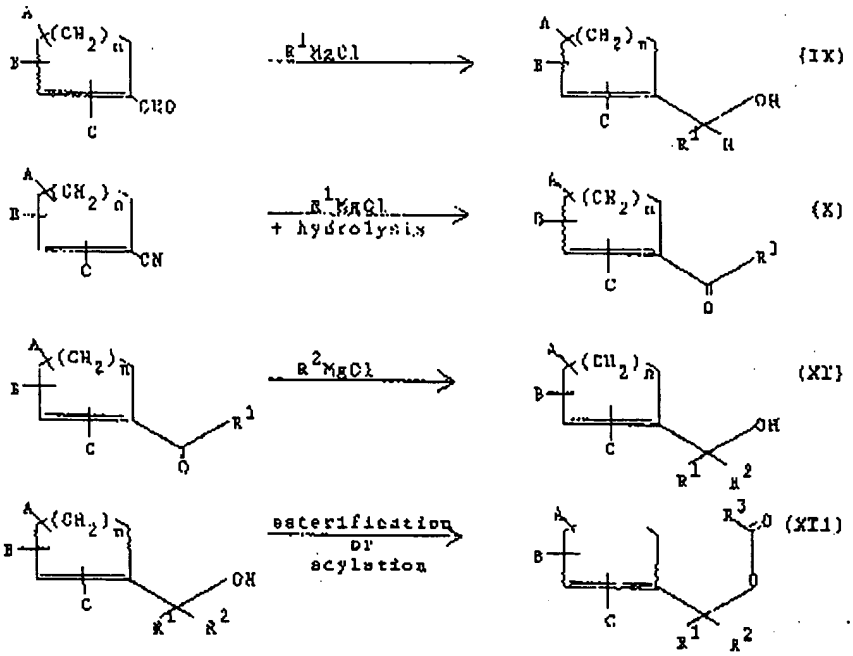
(IV)

In the above equations, A, B, C, R^1, R^2 and R^3 have the same meanings as set forth above and X is as indicated.

As shown in equation (I) a substituted or unsubstituted 1,3-diene is reacted with a substituted or unsubstituted α,β-unsaturated aldehyde or ketone to form the corresponding aldehydes or ketones. As shown in equation (IIa) this aldehyde or ketone is reacted with an appropriate Grignard reagent to form the corresponding secondary alcohol or, as shown in equation (IIb), is reacted with a metal hydride to form the corresponding cyclohex-3-en-1-yl methanol. Likewise, as shown in equation (III) the aldehyde or ketone is reacted with an appropriate Grignard reagent to form the corresponding tertiary alcohol. Equation (IV) illustrates the formation of the esters of this invention by, for instance, esterification of the primary and secondary alcohols and the acylation of the tertiary alcohol.

The compounds of formula (2) can be prepared as illustrated by the following equations:





In the above equations, A, B, C, R^1, R^2 and R^3 have the same meanings as set forth above.

As shown in equation (V) a substituted or unsubstituted cycloalkanone is reacted with hydrogen cyanide to form the corresponding cyanohydrins which are then dehydrated [equation (VI)] to form the corresponding α,β-unsaturated nitriles. Equation (VII) illustrates the reduction to the corresponding α,β-unsaturated cycloalkenyl carbaldehyde. In equations (VIII) and (IX) this aldehyde is reacted with a metal hydride or Grignard reagent respectively to form the corresponding primary or secondary alcohols. Finally, in equation (X), the cyanohydrin is reduced to the corresponding ketone by reaction with an appropriate Grignard reagent and hydrolysis. The ketone of equation (X) is reacted with another Grignard reagent, as in equation (XI) to form the tertiary alcohol. As in equation (IV), equation (XII) illustrates the esterification or acylation to form

the esters of this invention.

The instant compounds are capable of effectively counteracting malodors when utilized in small quantities and in many different mediums. For instance, use in room fresheners or room deodorants in the form of aerosols (sprays, etc.), liquids (wick type), solids (wax bases as in pomander, plastics, etc.), powders (sachets, dry sprays) and gels (solid gel sticks) are particularly preferred. Other illustrative uses are in clothes deodorants as applied by washing machine applications such as in detergents, powders, liquids, whiteners or fabric softeners or by other applications such as closet blocks, closet aerosol sprays, or clothes storage areas; in bathroom accessories such as paper towels, bathroom tissues, sanitary napkins, towellets, disposable wash cloths, disposable diapers, and diaper pail deodorants; in cleansers such as disinfectants and toilet bowl cleaners; in cosmetic products such as antiperspirant and underarm deodorants, general body deodorants in the form of powders, aerosols, liquids or solid, or hair care products such as hair sprays, conditioners, rinses, hair colors and dyes, permanent waves, depilatories, hair straighteners, hair groom applications such as pomade, creams, lotions, etc., medicated hair care products containing such ingredients as S-Selenium-sulfide, coal tar, salicylates, etc., or shampoos, or foot care products such as foot powders, liquids or colognes, after shaves and body lotions, or soaps and synthetic detergents such as bars, liquids, foams or powders; in odor control such as during manufacturing processes, such as in the textile finishing industry and the printing industry (inks and paper); in effluent control such as in processes involved in pulping, stock yard and meat processing, sewage treatment, or garbage disposal, or in product odor control as in textile finished goods, rubber finished goods, car fresheners, etc.; in agricultural and pet care products such as flea and

hen house effluents, and domestic animal and pet care products such as deodorants, shampoo or cleaning agents, or animal litter materials; in large scale closed air systems such as auditoriums, and subways and transport systems.

The amount of any such compound to be utilized has been found to be independent, in general, of the particular malodor involved. Likewise, the concentration of the malodor in the air containing it has been found to not affect the effective amount of the compound utilized. An amount effective to counteract the malodor should be used. The amount of any such compound however depends on the medium in which the compound is used, the temperature, humidity, air volume and air circulation. In general, such compounds are effective when present in air (containing the malodor) at levels as low as 0.01 mg./cubic meter of air. Of course, depending on the structure of the particular compound used, some compounds are more active than others. Any concentration above this amount will generally be effective. However, from a practical point of view, more than about 1.0 to 2.0 mg./cubic meter of air is probably unnecessary.

Particularly preferred compounds useful in the instant invention are those where the ring structure is cyclohexene, for instance, 3-cyclohexenylmethyl formate and 2-(cyclohex-3'-en-1'-yl)-propan-2-yl acetate.

Other illustrative compounds useful in the present invention are:

2-(Cyclopent-1'-en-1'-yl) propan-2-yl acetate
2-(Cyclopent-1'-en-1'-yl) propan-2-yl n-propionate
2-(Cyclopent-1'-en-1'-yl) propan-2-yl n-butyrate
2-(Cyclohept-1'-en-1'-yl) propan-2-yl acetate
2-(Cyclohept-1'-en-1'-yl) propan-2-yl n-propionate
2-(Cyclohept-1'-en-1'-yl) propan-2-yl n-butyrate

2-(Cyclooct-1'-en-1'-yl) propan-2-yl acetate
2-(Cyclooct-1'-en-1'-yl) propan-2-yl n-propionate
2-(Cyclooct-1'-en-1'-yl) propan-2-yl n-butyrate
1-(Cyclopent-1'-en-1'-yl) ethan-1-yl acetate
1-(Cyclopent-1'-en-1'-yl) ethan-1-yl n-propionate
1-(Cyclopent-1'-en-1'-yl) ethan-1-yl n-butyrate
1-(Cyclohept-1'-en-1'-yl) ethan-1-yl acetate
1-(Cyclohept-1'-en-1'-yl) ethan-1-yl n-propionate
1-(Cyclohept-1'-en-1'-yl) ethan-1-yl n-butyrate
1-(Cyclooct-1'-en-1'-yl) ethan-1-yl acetate
1-(Cyclooct-1'-en-1'-yl) ethan-1-yl n-propionate
1-(Cyclooct-1'-en-1'-yl) ethan-1-yl n-butyrate
4,6-Dimethylcyclohex-3-en-ylmethan-1-yl acetate
4,6-Dimethylcyclohex-3-en-ylmethan-1-yl n-propionate
4,6-Dimethylcyclohex-3-en-ylmethan-1-yl n-butyrate
2,5-Dimethylcyclohex-3-en-ylmethan-1-yl acetate
2,5-Dimethylcyclohex-3-en-ylmethan-1-yl n-propionate
2,5-Dimethylcyclohex-3-en-ylmethan-1-yl n-butyrate
3,5,5-Trimethylcyclohex-3-en-ylmethan-1-yl acetate
3,5,5-Trimethylcyclohex-3-en-ylmethan-1-yl n-propionate
3,5,5-Trimethylcyclohex-3-en-ylmethan-1-yl n-butyrate
2,2,4-Trimethylcyclohex-3-en-ylmethan-1-yl acetate
2,2,4-Trimethylcyclohex-3-en-ylmethan-1-yl n-propionate
2,2,4-Trimethylcyclohex-3-en-ylmethan-1-yl n-butyrate
2,6,6-Trimethylcyclohex-3-en-ylmethan-1-yl acetate
2,6,6-Trimethylcyclohex-3-en-ylmethan-1-yl n-propionate
2,6,6-Trimethylcyclohex-3-en-ylmethan-1-yl n-butyrate
2,6,6-Trimethylcyclohex-1-en-ylmethan-1-yl acetate
2,6,6-Trimethylcyclohex-1-en-ylmethan-1-yl n-propionate
2,6,6-Trimethylcyclohex-1-en-ylmethan-1-yl n-butyrate
2,2,4-Trimethylcyclohex-1-en-ylmethan-1-yl acetate
2,2,4-Trimethylcyclohex-1-en-ylmethan-1-yl n-propionate

2,2,4-Trimethylcyclohex-1-en-ylmethan-1-yl n-butyrate

2-Methylcyclohex-3-en-ylmethan-1-yl acetate

2-Methylcyclohex-3-en-ylmethan-1-yl n-propionate

2-Methylcyclohex-3-en-ylmethan-1-yl n-butyrate

4-Methylcyclohex-3-en-ylmethan-1-yl acetate

4-Methylcyclohex-3-en-ylmethan-1-yl n-propionate

4-Methylcyclohex-3-en-ylmethan-1-yl n-butyrate

4-Methylcyclohex-1-en-ylmethan-1-yl acetate

4-Methylcyclohex-1-en-ylmethan-1-yl n-propionate

4-Methylcyclohex-1-en-ylmethan-1-yl n-butyrate

5-Methylcyclohex-3-en-ylmethan-1-yl acetate

5-Methylcyclohex-3-en-ylmethan-1-yl n-propionate

5-Methylcyclohex-3-en-ylmethan-1-yl n-butyrate

6-Methylcyclohex-3-en-ylmethan-1-yl acetate

6-Methylcyclohex-3-en-ylmethan-1-yl n-propionate

6-Methylcyclohex-3-en-ylmethan-1-yl n-butyrate

4-Ethylcyclohex-1-en-ylmethan-1-yl acetate

4-Ethylcyclohex-1-en-ylmethan-1-yl n-propionate

4-Ethylcyclohex-1-en-ylmethan-1-yl n-butyrate

5-Ethylcyclohex-3-en-ylmethan-1-yl acetate

5-Ethylcyclohex-3-en-ylmethan-1-yl n-propionate

5-Ethylcyclohex-3-en-ylmethan-1-yl n-butyrate

4-Ethylcyclohex-3-en-ylmethan-1-yl acetate

4-Ethylcyclohex-3-en-ylmethan-1-yl n-propionate

4-Ethylcyclohex-3-en-ylmethan-1-yl n-butyrate

4-Isopropylcyclohex-1-en-ylmethan-1-yl acetate

4-Isopropylcyclohex-1-en-ylmethan-1-yl n-propionate

4-Isopropylcyclohex-1-en-ylmethan-1-yl n-butyrate

4-Isopropenylcyclohex-1-en-ylmethan-1-yl acetate

4-Isopropenylcyclohex-1-en-ylmethan-1-yl n-propionate

4-Isopropenylcyclohex-1-en-ylmethan-1-yl n-butyrate

[illegible]-ylcyclohex-3-en-ylmethan-1-yl acetate

4-Isopropylcyclohex-3-en-ylmethan-1-yl n-propionate
4-Isopropylcyclohex-3-en-ylmethan-1-yl n-butyrate
4-tert.Butylcyclohex-1-en-ylmethan-1-yl acetate
4-tert.Butylcyclohex-1-en-ylmethan-1-yl n-propionate
4-tert.Butylcyclohex-1-en-ylmethan-1-yl n-butyrate
4-tert.Butylcyclohex-3-en-ylmethan-1-yl acetate
4-tert.Butylcyclohex-3-en-ylmethan-1-yl n-propionate
4-tert.Butylcyclohex-3-en-ylmethan-1-yl n-butyrate
1-(Cyclohex-1'-en-1'-yl) ethan-1-yl acetate
1-(Cyclohex-1'-en-1'-yl) ethan-1-yl n-propionate
1-(Cyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate
1-(Cyclohex-3'-en-1'-yl) ethan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl) ethan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate
1-(Cyclohex-3'-en-1'-yl) propan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl) propan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl) propan-1-yl n-butyrate
2-(Cyclohex-3'-en-1'-yl) propan-2-yl acetate
2-(Cyclohex-3'-en-1'-yl) propan-2-yl n-propionate
2-(Cyclohex-3'-en-1'-yl) propan-2-yl n-butyrate
1-(Cyclohex-3'-en-3'-yl) butan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl) butan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl) butan-1-yl n-butyrate
1-(Cyclohex-3'-en-1'-yl)-2-methylpropan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl)-2-methylpropan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl)-2-methylpropan-1-yl n-butyrate
2-(Cyclohex-3'-en-1'-yl) butan-2-yl acetate
2-(Cyclohex-3'-en-1'-yl) butan-2-yl n-propionate
2-(Cyclohex-3'-en-1'-yl) butan-2-yl n-butyrate
1-(Cyclohex-3'-en-1'-yl) pentan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl) pentan-1-yl n-propionate

1-(Cyclohex-3'-en-1'-yl)-2-methylbutan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl)-2-methylbutan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl)-2-methylbutan-1-yl n-butyrate
1-(Cyclohex-3'-en-1'-yl)-3-methylbutan-1-yl acetate
1-(Cyclohex-3'-en-1'-yl)-3-methylbutan-1-yl n-propionate
1-(Cyclohex-3'-en-1'-yl)-3-methylbutan-1-yl n-butyrate
3-(Cyclohex-3'-en-1'-yl)-1-propen-3-yl acetate
3-(Cyclohex-3'-en-1'-yl)-1-propen-3-yl n-propionate
3-(Cyclohex-3'-en-1'-yl)-1-propen-3-yl n-butyrate
4-(Cyclohex-3'-en-1'-yl)-1-buten-4-yl acetate
4-(Cyclohex-3'-en-1'-yl)-1-buten-4-yl n-propionate
4-(Cyclohex-3'-en-1'-yl)-1-buten-4-yl n-butyrate
4-(Cyclohex-3'-en-1'-yl) but-2-en-4-yl acetate
4-(Cyclohex-3'-en-1'-yl) but-2-en-4-yl n-propionate
4-(Cyclohex-3'-en-1'-yl) but-2-en-4-yl n-butyrate
4-(Cyclohex-3'-en-1'-yl)-3-methylbut-1-en-4-yl acetate
4-(Cyclohex-3'-en-1'-yl)-3-methylbut-1-en-4-yl n-propionate
4-(Cyclohex-3'-en-1'-yl)-3-methylbut-1-en-4-yl n-butyrate
5-(Cyclohex-3'-en-1'-yl) pent-2-en-5-yl acetate
5-(Cyclohex-3'-en-1'-yl) pent-2-en-5-yl n-propionate
5-(Cyclohex-3'-en-1'-yl) pent-2-en-5-yl n-butyrate
1-(2'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl acetate
1-(2'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate
1-(2'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate
1-(4'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl acetate
1-(4'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate
1-(4'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate
1-(6'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl acetate
1-(6'-Methylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(3',5'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(2',5'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(2',5'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(4',6'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(4',6'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(4',6'-Dimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(3',5',5'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(3',5',5'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(3',5',5'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(2',6',6'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(2',6',6'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(2',6',6'-Trimethylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(2',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(2',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-propionate

1-(2',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(4',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(4',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-propionate

1-(4',6',6'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(2',4',4'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(2',4',4'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-propionate

1-(2',4',4'-Trimethylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(4'-Ethylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(4'-Ethylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(4'-Ethylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(4'-Ethylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(4'-Ethylcyclohex-1'-en-1'-yl) ethan-1-yl n-propionate

1-(4'-Ethylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(4'-Isopropylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(4'-Isopropylcyclohex-1'-en-1'-yl) ethan-1-yl n-propionate

1-(4'-Isopropylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(4'-Isopropylcyclohex-3'-en-1'-yl) ethan-1-yl acetate

1-(4'-Isopropylcyclohex-3'-en-1'-yl) ethan-1-yl n-propionate

1-(4'-Isopropylcyclohex-3'-en-1'-yl) ethan-1-yl n-butyrate

1-(4'-tert.Butylcyclohex-1'-en-1'-yl) ethan-1-yl acetate

1-(4'-tert.Butylcyclohex-1'-en-1'-yl) ethan-1-yl

1-(4'-tert.Butylcyclohex-1'-en-1'-yl) ethan-1-yl n-butyrate

1-(2'-Methylcyclohex-3'-en-1'-yl) propan-1-yl acetate

1-(2'-Methylcyclohex-3'-en-1'-yl) propan-1-yl n-propionate

1-(2'-Methylcyclohex-3'-en-1'-yl) propan-1-yl n-butyrate

2-(2'-Methylcyclohex-3'-en-1'-yl) propan-2-yl acetate

2-(2'-Methylcyclohex-3'-en-1'-yl) propan-2-yl n-propionate

2-(2'-Methylcyclohex-3'-en-1'-yl) propan-2-yl n-butyrate

1-(2'-Methylcyclohex-3'-en-1'-yl) butan-1-yl acetate

1-(2'-Methylcyclohex-3'-en-1'-yl) butan-1-yl n-propionate

1-(2'-Methylcyclohex-3'-en-1'-yl) butan-1-yl n-butyrate

The following examples are given to illustrate the instant invention in detail. It is to be understood that the specific details given in the examples are not to be construed as limiting the scope of the invention. The symbol "mg./cu. meter" refers to the weight (in milligrams) of material present in one cubic meter of air.

Example 1

3-CYCLOHEXENYLMETHYL FORMATE

A mixture of 33.6 g. (0.3 moles) of 3-cyclohexene methanol and 46.0 g. (1 mol) 97% formic acid was refluxed for one hour. After cooling to room temperature the reaction mixture was poured into ice water and the organic material extracted with ether. The ether extract was washed with water, sodium bicarbonate, water and finally brine and dried overnight over molecular sieves A4. Filtering to remove the drying agent, washing the residue with ether and combining with the filtrate and distilling off the ether afforded 38.2 g. (90.8%) of crude material of 94.2% purity by GLC. It was purified by distillation through a short Vigreux-column. The product, 3-cyclohexenylmethyl formate, a colorless mobile liquid, had b.p. 84°C/18 mm of Hg. n_D^{25} 1.4628. Yield 35.5 g. (84.9%) having a 96.1% purity. The impurity is unreacted alcohol.

Odor: Powerful green, fruity, chemical

Example 2

3-CYCLOHEXENYLMETHYL ACETATE

To a mixture of 33.6 g. (0.3 moles) 3-cyclohexene methanol and 34.0 g. (0.33 moles) acetic acid was added 100 mg. p-toluene sulfonic acid and the mixture left at room temperature for 20 hours. Then 2 ml. water was added, and after one hour 1 g. sodium acetate and the mixture poured in 300 ml. water. The organic layer was separated. The aqueous layer extracted

thoroughly with water, sodium bicarbonate solution, water, and brine and dried over molecular sieves A4 overnight. Using a similar procedure as in example 1 afforded 44.1 g. of crude (95.3%), n_D^{25} 1.4574, purity 93.2% by GLC. The low boiling impurity was removed by distillation through a short Vigreux-column. The product, 3-cyclohexenylmethyl acetate, a colorless mobile liquid, had b.p. 96°C./18 mm. of Hg, n_D^{25} 1.4576, yield 40.3 g. (87.1%). Purity was 100% by GLC.

Odor: Powerful green, fruity, citrus.

Example 3

3-CYCLOHEXENYLMETHYL PROPIONATE

To a mixture of 33.6 g. (0.3 moles) 3-cyclohexene methanol and 44.3 g. (0.33 moles) propionic anhydride was added 100 mg. p-toluene sulfonic acid and the solution left at room temperature overnight. Using the same recovery procedure as in example 2 gave 51.2 g. (~100%) of crude, purity 99%, n_D^{25} 1.4545, containing a trace anhydride. It was purified by distillation through a Vigreux-column. The product, 3-cyclohexenyl-methyl propionate, was collected after a forerun, b.p. 84-108°C./18 mm. of Hg., n_D^{25} 1.4312 was removed. It was a colorless, fragrant mobile liquid, b.p. 108-110°C./18 mm. of Hg., n_D^{25} 1.4566, Yield 43.2 g. = 85.6%. Purity 100% by GLC.

Odor: Green, floral, rosy, styrax-type.

Example 4

3-CYCLOHEXENYLMETHYL ISOBUTYRATE

To a mixture of 28.0 g. (0.25 moles) 3-cyclohexene methanol and 39.6 g. isobutyric anhydride (0.25 moles) was added 100 mg. p-toluene sulfonic acid and the mixture left at room temperature overnight. Using the same recovery procedure as in example 2 gave 42.6 g. (98.7% of crude product, n_D^{25} 1.4540, purity 98.7% by GLC. It was distilled through a Vigreux-column

colorless, fragrant mobile liquid. b.p. 102°C./9.5 mm. of Hg., n_D^{25} 1.4540, Yield 39.2 g = 86.0% of 99.7% purity by GLC.

Odor: Floral, spicy, balsamic, lily-cinnamic.

Example 5

3-CYCLOHEXENYLMETHYL BUTYRATE

To a mixture of 28.0 g. (0.25 moles) 3-cyclohexene-methanol and 39.6 g. (0.25 moles) n-butyric anhydride was added 100 mg. p-toluene sulfonic acid and the mixture reacted and using the same recovery procedure as in example 2 gave 41.3 g. (90.6%) of crude, n_D^{25} 1.4565, purity 96.4% by GLC. This was distilled through a short Vigreux-column to give: b.p. up to 108°C./9.5 mm. of Hg., n_D^{25} 1.4564, 4.1 g (contains low boilers): b.p. 108°C./9.5 mm. of Hg., n_D^{25} 1.4570, 34.4 g = 75.5% (main cut). The product, 3-cyclohexenylmethyl butyrate, is a colorless fragrant floral, fatty odorous liquid, purity 98.6% by GLC.

Example 6

2-(CYCLOHEX-3'-EN-1'-YL)-2-PROPYL ACETATE

5.7 g. (0.04 moles) of dimethylcyclohex-3'-enyl carbinol were mixed with 5 g. acetic anhydride, 0.1 g. 85% phosphoric acid added and the mixture left at room temperature for 48 hours. It then was poured into ice water and the organic material isolated as in example 2. The crude product, 2-(cyclohex-3'-en-1-yl)-2-propyl acetate, a yellow liquid was distilled (take over) to give 5.3 g. (72%) of colorless product, having a lavender, lavandin, bergamot and spicy odor, b.p. 75°C./3.5 mm. of Hg, n_D^{25} 1.4630. 99+% purity by GLC.

Example 7

The following malodor concentrate was prepared:

Bathroom Malodor Concentrate

Component	Parts by Wt.
Skatole	0.91
β-thionaphthol	0.91
95% aqueous solution of thioglycolic acid	21.18
n-caproic acid	6.00
p-cresyl isovalerate	2.18
N-methyl morpholine	6.00
Dipropylene glycol	62.82

Aerosol cans were prepared with the above malodor with the following concentrations:

Bathroom Malodor Aerosol

Component	Parts by Wt.
Bathroom Malodor Concentrate	0.1
Dipropylene glycol	4.9
Propellant	
a. trichloromonofluoromethane	47.5
b. dichlorodifluoromethane	47.5

A "Spice for Cologne" fragrance was selected for use in testing the malodor counteractant ability of the compounds tested. The "Spice for Cologne" fragrance contained the following ingredients:

Ingredients	Parts by Wt.
Lavandin Abrialis Oil	60
Amyl Cinnamic Aldehyde	20
Amyl Salicylate	150
Benzyl Acetate	30
Linalool	30
Cedarwood Oil	10
Geraniol	130
Isopulegol	60
Methyl Anthranilate (10% by weight solution in dipropylene glycol)	20
Musk Xylol	60
Coumarin	50
Phenyl Ethyl Acetate	30
Terpinyl Acetate	100
Cinnamon Leaf Oil	40
Petitgrain Oil SA	130
Phenyl Acetaldehyde Dimethyl Acetal	15
Cinnamic Alcohol	5
	1000

Aerosol cans were prepared with the above fragrance composition with the compounds to be tested being present as a malodor counteractant as follows:

Ingredient	% by Wt.
"Spice for Cologne"	0.45
Compound to be tested	0.05
Propellant	
a. trichloromonofluoromethane	49.75
b. dichlorofluoromethane	49.75
	100.00

A test chamber having inside dimensions of 3.33 x 3.64 x 2.42 (meters) with a total volume of 29.9 cubic meters, having

an access door and an exhaust fan was provided. The capacity of the exhaust fan was 14.3 cubic meters/min. In order to insure satisfactory evacuation the exhaust fan was operated for five minutes between tests and an olfactory check was made to determine if any residual odor could be detected prior to conducting the next test.

After the test chamber had been suitably evacuated the bathroom malodor was sprayed from the aerosol can for about five seconds. After a delay of from 10-15 seconds the fragrance composition aerosol was sprayed for about five seconds (five seconds being an average time such an aerosol would usually be used by a housewife). One minute thereafter a 2 member panel (consisting of 1 person skilled in perfumery and odor evaluation and 1 person having no such skills but being familiar with fragrances in general) entered the test chamber, performed an olfactory evaluation for detection of the malodor and recorded their observations. All tests were performed with neither member of the panel being aware of the identity of the material being tested.

Based on the flow rate through the valve utilized in the aerosol can the approximate amount of aerosol, containing the malodor concentrate, introduced into the test chamber is 267 mg./cu. meter.

The amount of aerosol containing the fragrance compositions introduced into the test chamber is approximately 260 mg./cu.meter.

The compounds indicated in Table 1 were incorporated into "Spice for Cologne" fragrance composition aerosol cans according to the above procedure and, using the above test procedures, they were tested for their ability to counteract the bathroom malodor. The results are shown in Table 1.

TABLE 1

Compound	Activity[+]
3-Cyclohexenylmethyl Formate	U*
3-Cyclohexenylmethyl Acetate	U
3-Cyclohexenylmethyl Propionate	V
3-Cyclohexenylmethyl Isobutyrate	U
3-Cyclohexenylmethyl Butyrate	U
2-(Cyclohex-3'-en-1'-yl)-2-Propyl Acetate	U*

[+] Ability of compound to counteract the malodor according to the following scale:

U* "Outstanding" - Fresh air effect pronounced and producing extremely light or no residual odor at all.

U "Excellent" - Fresh air effect and light and pleasant residual background odor.

V "Very good" - No fresh air effect but total abatement of malodors, variable, but not high residual background odor.

W "Good" - Only traces of malodor, often of changed quality, remain. Residual background odor acceptable to pleasant, not too strong.

X "Fair" - Original malodor clearly discernable but of low intensity. Residual background odor acceptable at best.

Y "Poor" - Original malodor somewhat reduced in intensity, but dominates. Overall residual background odor unpleasant to unacceptable.

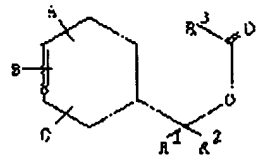
Z "No Activity".

These are particularly surprising results because when the "Spice for Cologne" fragrance composition aerosol without such compounds is tested both members of the panel detected the presence of the malodor.

While the invention has been described herein with regard to certain specific embodiments, it is not so limited. It is to be understood that variations and modifications thereof may be made by those skilled in the art without departing from the spirit and scope of the invention.

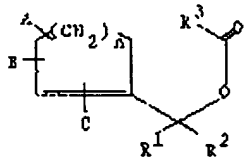
The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A composition to be used to counteract malodors wherein an amount, effective to counteract the malodor, of a compound represented by the structural formulae



(1)

or



(2)

wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen, a lower alkyl having from 1 to 5 carbon atoms or a lower alkenyl having from 3 to 5 carbon atoms, provided that the sum of the carbon atoms in A, B and C is no more than 7,

R^1 and R^2 each independently represent hydrogen or a lower alkyl or alkenyl having from 1 to 5 carbon atoms,

R^3 represents hydrogen or a lower alkyl or alkenyl having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R^1 or R^2 plus R^3 is no more than 10,

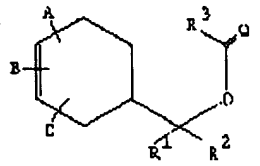
is present in the composition.

2. A composition according to Claim 1 wherein the malodor counteractant compound is present in an amount sufficient to provide at least about 0.01 mg./cu.meter of air containing the malodor.

3. A composition according to Claim 1 which is a room freshener.

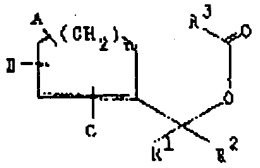
4. A composition according to Claim 3 which is utilized in the form of an aerosol.

5. A method of treating malodors to alleviate their offensive odors which comprises treating the air containing the malodor with an amount, effective to counteract the malodor, of a compound represented by the structural formulae



(1)

or



(2)

wherein

n is an integer of from 1 to 4,

A, B and C each independently represent hydrogen, a lower alkyl having from 1 to 5 carbon atoms or a lower alkenyl having from 3 to 5 carbon atoms, provided that the sum of the carbon atoms in A, B and C is no more than 7,

R^1 and R^2 each independently represent hydrogen or a lower alkyl or alkenyl having from 1 to 5 carbon atoms,

R^3 represents hydrogen or a lower alkyl or alkenyl having up to 6 carbon atoms, provided that the sum of the larger number of carbon atoms in either R^1 or R^2 plus R^3 is no more than 10.

6. A method according to Claim 5 wherein the malodor counteractant compound is provided in an amount sufficient to provide at least 0.01 mg./cu/meter of air containing the malodor.

7. A method according to Claim 5 wherein the malodor counteractant compound is utilized in the form of a room freshener.

8. A method according to Claim 7 wherein the room freshener is introduced as an aerosol.

9. A composition according to Claim 1 wherein n is 2.

10. A method according to Claim 5 wherein n is 2.

11. A composition according to Claim 9 wherein the malodor counteractant compound is 3-cyclohexenylmethyl formate, 3-cyclohexenylmethyl acetate, 3-cyclohexenylmethyl propionate, 3-cyclohexenylmethyl isobutyrate, 3-cyclohexonylmethyl butyrate, or 2-(cyclohex-3'-en-1'-yl)-2-propyl acetate.

12. A method according to Claim 10 wherein the malodor counteractant compound is 3-cyclohexenylmethyl formate, 3-cyclohexenylmethyl acetate, 3-cyclohexenyl propionate, 3-cyclohexenylmethyl isobutyrate, 3-cyclohexenylmethyl butyrate, or 2-(cyclohex-3'-en-1'-yl)-2-propyl acetate.

13. A composition according to Claim 1, 2 or 3 wherein each of substituents A, B and C is a hydrogen atom.

14. A composition according to Claim 4, or 9 wherein each of substituents A, B and C is a hydrogen atom.

15. A method according to Claim 5, 6 or 7 wherein each of substituents A, B and C is a hydrogen atom.

16. A method according to Claim 8 or 10 wherein

17. A composition according to Claim 1, 2 or 3 wherein each of R_1 and R_2 is hydrogen or an alkyl group of 1-5 carbon atoms.

18. A composition according to Claim 4 or 9 wherein in each of R_1 and R_2 is hydrogen or an alkyl group of 1-5 carbon atoms.

19. A method according to Claim 5, 6 or 7 wherein each of R_1 and R_2 is hydrogen or an alkyl group of 1-5 carbon atoms.

20. A method according to Claim 8 or 10 wherein each of R_1 and R_2 is hydrogen or an alkyl group of 1-5 carbon atoms.

21. A composition according to Claim 1, 2 or 3 wherein each of R_1 and R_2 is hydrogen or methyl.

22. A composition according to Claim 4 or 9 wherein each of R_1 and R_2 is hydrogen or methyl.

23. A method according to Claim 5, 6 or 7 wherein wherein each of R_1 and R_2 is hydrogen or methyl.

24. A method according to Claim 8 or 10 wherein each of R_1 and R_2 is hydrogen or methyl.

25. A composition according to Claim 1, 2 or 3 wherein R_3 is hydrogen or lower alkyl.

26. A composition according to Claim 4 or 9 wherein R_3 is hydrogen or lower alkyl.

27. A method according to Claim 5, 6 or 7 wherein R_3 is hydrogen or lower alkyl.

28. A method according to Claim 8 or 10 wherein R_3 is hydrogen or lower alkyl.

29. A composition according to Claim 1, 2 or 3 where the compound is formula 1.

30. A composition according to Claim 4 where the

31. A method according to Claim 5, 6 or 7 where the compound is formula 1.

32. A method according to Claim 8 or 10 where the compound is formula 1.

33. A composition according to Claim 1, 2 or 3 where the compound is formula I, and wherein each of substituents A, B and C is a hydrogen atom, each of R_1 and R_2 is hydrogen or methyl and R_3 is hydrogen or lower alkyl.

34. A composition according to Claim 4 where the compound is formula 1, and wherein each of substituents A, B and C is a hydrogen atom, each of R_1 and R_2 is hydrogen or methyl and R_3 is hydrogen or lower alkyl.

35. A method according to Claim 5, 6 or 7 where the compound is formula 1, and each of substituents A, B and C is a hydrogen atom, each of R_1 and R_2 is hydrogen or methyl and R_3 is hydrogen or lower alkyl.

36. A method according to Claim 8, where the compound is formula 1 and each of substituents A, B and C is a hydrogen atom, each of R_1 and R_2 is hydrogen or methyl and R_3 is hydrogen or lower alkyl.